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III.

THE SPECTRUM OF HYDROGEN IN THE REGION OF EXTREMELY SHORT WAVE-LENGTH.

BY

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WITH SIX PLATES.

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CONTENTS.

THE SPECTRUM OF HYDROGEN IN THE REGION OF EXTREMELY SHORT WAVE-LENGTH.

INTRODUCTION.

In a preliminary paper[1] the author has given the wave-length of more than one hundred and thirty lines in the region of the spectrum lying between the values 1850 and 1030 tenth metres. It is the object of the present paper to compare the results obtained by the author with those given by Schumann; to describe the apparatus used in this research and to call attention to some new facts which have come to light since the publication of the first notice. The description has been made with some minuteness in the hope that an exact knowledge of the conditions necessary to success may prove of value to investigators who work in this field. Some attention has also been given to earlier and imperfect forms of the apparatus. For the author wishes, by flagging the pits into which he has fallen, to prevent other investigators from similar accidents.

The improvement over the method of Schumann which characterizes this research consists in the introduction of a concave diffraction grating in place of fluorite prism and lenses, thus permitting the measurement of wave-lengths. The object of continuing the work has been to improve the accuracy of the measurements and to eliminate from the radiation obtained from a hydrogen tube those frequencies which were due to impurities.

As it is unsafe to rely upon a process of extrapolation even with a grating spectrum, the two-slit method described in a previous paper[2] was employed. The spectroscope has been altered in construction to permit of all the adjustments required for this method and finally the photographic plate itself has been bent to agree in curvature with the arc of the circle on which the spectrum is in theory formed. Very considerable increase in accuracy has thus been gained. The grating with which the work has been done possesses one extremely strong first

[1] Astrophysical Journal, Vol. XIX, No. 4, 1904.
[2] Physical Review, Vol. XVI, No. 5, 1903.

spectrum, in fact it is to its brilliancy that the success of the research is due. In spite of the feebleness of the other spectra, however, it has been found possible to obtain many of the stronger lines between λ 1550 and λ 1250 in the second spectrum. Their measurement therefore forms a valuable check on the numbers obtained by the two-slit method.

The elimination of the lines due to impurities from the spectrum of hydrogen necessitates the study of the spectrum of air. As has been set forth in the earlier paper it is found most convenient to fill the spectroscope itself with pure hydrogen; in fact if the lines of the shortest wave-length are to be obtained the light-path must be entirely in this medium. No window between discharge tube and spectroscope is permissible. When, however, the spectrum of a gas other than hydrogen is to be studied a window of fluorite must separate the discharge tube from the spectroscope. The extent of the spectrum is limited, therefore, by the transparency of colorless fluorite and the absorption of this substance has formed a necessary part of this research. As a matter of fact even fluorite of the best quality was found to absorb all light below wave-length λ 1200; the study of the spectra of gases other than hydrogen therefore terminates with this value.

In view of the fact that Schumann made use of two fluorite lenses and a fluorite prism it seemed extremely probable that his spectrum does not extend below wave-length λ 1200. To test the matter the plates published in the Smithsonian Contributions to Knowledge No. 1413, have been compared with the normal spectrum obtained during this research, and it has been found possible to identify a great majority of the hydrogen lines in this prism spectrum with lines measured by the author. Two important results follow. First, a scale of wave-lengths has been attached to the Schumann spectrum, as shown in the half-tone reproductions at the end of this memoir. Second, as the line of lowest wave-length visible in Schumann's plates has the value λ 1267, the present limit λ 1030 establishes a considerable extension of the spectrum.

Since the effect of change in the electrical conditions under which a spectrum is produced is extremely important, the question of the existence of a secondary spectrum of hydrogen in the region of short wave-lengths has been examined. No such spectrum appears to exist; that is to say, there is but one hydrogen spectrum between λ 2000 and λ 1200.

The following pages contain a detailed account of the work of which the foregoing paragraphs may serve as an outline.

THE SPECTROSCOPE.

The apparatus consists of two parts, the spectroscope itself and the vacuum receiver in which it is enclosed. The spectroscope is formed of a drawn brass tube 9.1 cm. in internal diameter, 96 cm. long, and 1.5 mm. thick, one end of which is provided with an arrangement for holding the grating while the other end carries the plate-holder and slits. The grating mounting consists of a square brass plate pivoted to turn about a vertical axis. The grating is held against this plate by springs, while screws through the back of the plate permit of the necessary adjustment about a horizontal axis. At the end not occupied by the grating a draw tube fits into the large tube. Upon the end of this draw tube are mounted the slits and plate-holder in a manner shown in Plate VI, figs. 1, 2, and 4, and which may be described as follows: A circular brass disc closes the end of the draw tube and is pivoted about the points *A A*, fig. 4. The motion of this disc is regulated by the screws *X X*. Upon the disc are mounted the two slits *S S*. The width of the slits is controlled by the usual screw adjustment. In order to be able to adjust the slits parallel to each other one of them is mounted in a tube which turns in the disc; the amount of this twist is regulated by the lever *L*.

The plate-holder *C* is so constructed that several photographs may be taken without withdrawing it from the apparatus. To this end the disc carries two ways *D D* in which the plate-holder slides. The position of the holder in the ways is controlled by the lever *E*, pivoted about the point *F*. One end of this lever carries the pin *G*, while the other end is provided with an iron armature *H*. The pin *G* engages one of the horizontal rods, *I*, and thus holds the plate-holder in position. To shift this position it is only necessary to swing the lever about *F* by means of a magnet exterior to the apparatus, the pin *G* then slips past one of the rods, *I*, and the plate-holder falls by an amount corresponding to the distance between two rods. The plate-holder is designed to permit the plate to be bent to the arc of a circle of given curvature. To this end it is constructed in two parts, the outside case *C* and the movable form *M*. The form (shown withdrawn from the case, fig. 3) carries two strips *N N*, whose under sides are cut to the desired curvature, the ends of these strips project beyond the main body of the form. The plate *P* is slipped into the form and is tangent, when unbent, to the curved strips at their middle point. The form is then drawn into the case by means of the screws *O O*, the ends of the plate come up against the shoulders *R R*, and as the screws are tightened the plate is bent to coincide with the strips *N N*.

The apparatus is so constructed that the curve to which the plate is bent passes through the slits. Light has access to the plate through a slot T cut in the disc, which slot also serves as a diaphragm for the spectrum. A sleeve, U, shields the plate from scattered light; and to reduce the reflection from the walls of the tube a set of circular diaphragms are provided. The whole system, draw tube and large tube, are blackened inside by the usual process. In the early work it was proposed to enclose the spectroscope as above described in a large glass tube, but owing to the difficulty of closing such a receiver air-tight, and owing to the great liability of tubes of this size to break, the plan was abandoned. The receiver at present in use consists of a drawn brass tube 11.3 cm. in diameter, 110 cm. long, and 1.8 mm. thick. It is provided with two flanges, one at each end, cut from sheet brass and soldered to the tube. The flange at the end destined to be nearest the grating is closed by a circular brass plate, ground true, some 17 cm. in diameter. Plates of two kinds have been used to close the other end of the receiver. In the simpler form shown in Plate VII, fig. 2, a circular brass disc was only pierced by the two holes destined to admit light to the slits of the spectroscope. In the more complex form, fig. 4, a hand hole is also provided through which the plate-holder may be introduced. This hole is 6.2 cm. in diameter and is closed air-tight by a conical plug. In order to give this plug a sufficient bearing, a sleeve some 4.5 cm. high is attached to the face plate. An inlet tube inserted about midway down the length of the receiver serves to exhaust the air; a wooden frame holds the apparatus horizontal. To facilitate the handling and development of the dry plates the end of the receiver is inserted in a small dark room. Plate VII, fig. 1, shows the appearance of this arrangement. Into the receiver thus described the spectroscope is slipped, small hard rubber-legs hold it in a central position. Plate VII, fig. 3, shows the end of the apparatus with the face plate removed.

The concave grating with which the work has been done was ruled in 1903 on the improved engine at Johns Hopkins University. The material is the usual speculum metal, the radius 97 cm.; there are 15,028 lines to the inch. The diamond point was selected with the object of throwing as much of the light as possible into one spectrum. To the great success which attended this effort the results of the work are due, for the instrument possesses one first spectrum of extreme brilliancy.

As the experiment is carried on in an atmosphere of hydrogen the preparation of the gas is an important factor. Zinc and hydrochloric acid of the greatest commercial purity obtainable are used. The gas is passed over potassium hydrate and collected over distilled water. Before the gas is admitted to the spectroscope it is dried over calcium chloride and phosphorous pentoxide. The drying tubes are protected at

each end by a stop-cock, thus the gas does not flow through the system directly but stands over the material for some minutes before entering the spectroscope. The perfect dryness of the gas is necessary for the success of the work. All connections between hydrogen apparatus, tubes, and spectroscope are of glass. The exhaustion is effected by a "Geryk" oil pump driven by an electric motor, the pressure is read by a McLeod gauge properly protected by drying tubes. Here again all connections are of glass. All air admitted to the spectroscope is passed through a separate set of drying tubes. These precautions have been found necessary to prevent the appearance of absorption bands. The joint between the brass receiver and the system of glass tubing is made by a glass sleeve sealed with De Kotenski cement. Though this form of joint leaves something to be desired, nothing better has as yet been devised.

The use of a discharge tube separated from the receiver by a fluorite window necessitates a separate pumping system, for the tube must be exhausted apart from the receiver and filled with the gas to be studied. For this purpose a mercury pump by Kiss of Buda-Pesth has been used. The hydrogen is made electrolytically from a solution of barium hydrate and is dried over phosphorous pentoxide.

The form of the discharge tube depends upon the manner of making the experiment. If the tube is to communicate directly with the receiver so that the whole apparatus is filled from the receiver with hydrogen, the usual form of capillary tube with ring electrodes is employed. The dimensions in a typical case were as follows: Length of capillary 6.4 cm., internal diameter 2.5 mm., diameter of electrodes 1.6 cm., distance of mouth of tube to electrode 4.5 cm. This last dimension is of special importance, since if it be made too small the discharge from the tube spreads into the receiver and produces fog, and if it be made too large intensity of illumination is sacrificed.

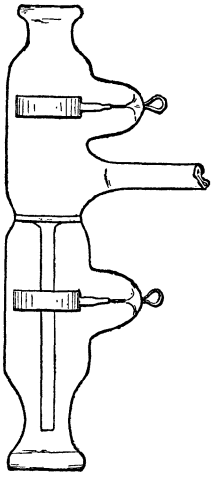


FIG. 1.

If the tube is to be separated from the receiver by a window and is to be separately exhausted, a special form is used. (Fig. 1.) Here the end of the internal capillary is brought as near the fluorite window as may be without undue heating. A device of this type not only brings the source of light near to the slit of the spectroscope but reduces the absorption in the tube itself to a minimum. The last advantage is a most important one in dealing with gases such as air which absorb strongly. The electrodes in both forms of tube were usually of aluminum, but iron and copper have also been tried.

ADJUSTMENT.

After the spectroscope is placed in the receiver the grating is turned until that part of the first spectrum to be investigated falls on the photographic plate. The arrangement of two slits serves a double purpose, as by it either the method of shifted spectra or the second spectrum comparison method may be used, without altering the position of the grating. For no matter which method is to be employed the grating is so placed that light from the right hand slit gives the region of short wave-length in the first spectrum, while by illuminating the left hand slit a shifted first spectrum is obtained superposed upon a shifted second spectrum. The dimensions of the apparatus are such that when the longest wave-length which falls on the plate from the right hand slit lies in the region of 1900 Ångströms, the longest wave-length in the shifted first spectrum has a value of about 3100 Ångströms. Observation of lines in the shifted spectrum serves, therefore, as a simple test of the exact position of the grating. When this position has once been reached the grating end of the receiver is closed, a very little vaseline being used in the joint, and the edge is looted with shellac or De Kotęnski cement of the softer kind. It next becomes necessary to prepare the other face plate. If the shifted spectrum method is to be employed, this process consists in covering that hole which is to admit light to the left hand slit with a quartz window and to seal the discharge tube over the right hand opening. This last adjustment is a tedious one, for the mouth of the discharge tube must be ground at such an angle that the capillary lies in the line determined by the slit and the grating centre. This can only be done by trial. When the correct angle has been arrived at the tube is fastened to the face plate with De Kotenski cement. To insure a strong joint the brass surface must be heated during the operation. The face plate with the tube thus attached is rubbed evenly with a little white vaseline and applied to the flange of the receiver. Here great care must of course be used that the tube is in line with the slit. To facilitate this operation, tubes of both forms are made double ended, that is, they have a quartz window by means of which it is possible to look through the capillary to the slit and thus assure correct alinement. Once in position the plate is clamped and the edge looted with cement. Plate VII, fig. 4, illustrates the appearance of the more improved form of plate and discharge tube in position.

The fact that the end of the receiver is in a dark closet permits the plate-holder to be placed in the ways of the spectroscope through the hand-hole without danger of fog. The hand-hole is next closed by the conical plug and around the edge of the joint a little shellac is spread. The apparatus is now ready to exhaust. If no window

is used between discharge tube and spectroscope both parts of the apparatus are of course exhausted together and both are filled with hydrogen together. If a window separates the two, the tube must be exhausted by the mercury pump and filled from the separate supply of hydrogen. In either case the most laborious part of the adjustment lies still ahead, for the spectra from both slits must be in focus at the same time and the position of the plate-holder can only be determined by trial. It is therefore necessary to take a series of spectrographs, removing the face plate after every trial in order to change the adjustment of the spectroscope, and replacing the plate on each occasion air-tight in order to exhaust and fill with hydrogen. As can be easily understood from the figure, that the conditions of adjustment should be fulfilled both slits must lie on the circle whose diameter is the grating's radius of curvature and the plate must form a part of the arc of this circle. By construction, the curve to which the plate is bent passes through the slits. There are then two degrees of freedom of adjustment, the draw tube can be run in and out and the disc can be turned about the axis $A\,A$; these two motions will suffice to bring the slits and plate into their correct theoretical positions.

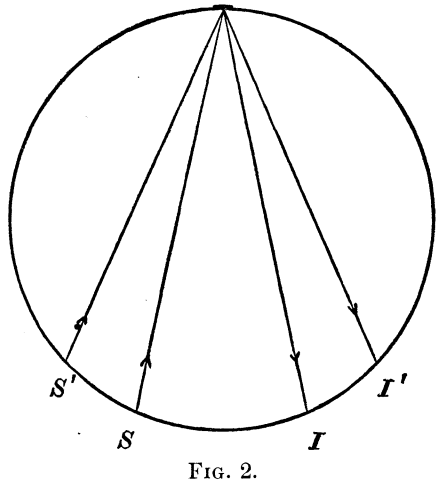


FIG. 2.

Tedious as is the method of trial above described it has seemed better to adopt it rather than to complicate the apparatus by the introduction of devices to regulate the focus from outside the receiver. Such devices might permit the focus to be changed without admitting the air, but the author is not at present prepared to face the problem of moving joints which must be maintained air-tight. Once the spectroscope is in adjustment the face plate, if it is of the improved form, can remain permanently in place.

As regards pumping the apparatus, and as to the extent to which it is necessary to wash with hydrogen with a direct connected discharge tube, the following example may be of interest. The receiver and drying tubes were first exhausted to .7 mm. of mercury. The tubes were then shut off and filled with hydrogen; after the gas had stood over the drying material for two or three minutes it was admitted to the receiver. A second filling of hydrogen was let into the drying tubes and in turn run into the receiver. The tubes are of such a capacity that two fillings raise the pressure by about 15 cm. of mercury. The pump was then applied and the pressure reduced to .45 mm.; hydrogen was admitted, the pump again applied until the pressure again

reached about .45 mm. and an equal amount of hydrogen was for the third time admitted. It was usual to repeat this process of washing at least four times before a photograph was tried.

In making the exposure the end on tube was excited by the transformer described in the previous paper. For the best results that pressure was chosen which gave a brilliant discharge in the tube without being so low as to permit the glow to spread from the tube into the spectroscope. The best value for the pressure under the conditions was in the neighborhood of 1.5 mm. The receiver was generally pumped to this pressure before the tube was excited.

In a plate such as that previously published, where several spectra appear upon one negative, it was usual to allow a fresh supply of hydrogen to enter the receiver between each exposure. Thus after the plate-holder has been lowered by the magnetic device the receiver is repumped. It is just to suppose that the gas in the apparatus is much purer during the last exposure than during the first. The effect of this increased purity upon the nature of the spectra themselves has been noted in the former article, unfortunately the reproduction did not show the effect at all well, though it was extremely clear upon the original negative.

The process of washing, pumping, and rewashing is of necessity a tedious one and generally occupied the better part of a day. Schumann has observed that the appearance of the hydrogen spectrum in its visible part was no criterion of its purity as observed in the region of short wave-length. It may be of interest to add, nevertheless, that the discharge tube when properly washed with hydrogen showed the many line spectrum of that gas in a state of considerable purity. The appearance of air lines was always a sure warning, if a discharge tube without a window was used, that the spectrum on the photographic plate would be extremely feeble.

In work of this kind it is found almost impossible to make the receiver absolutely air-tight. In fact some of the most successful of the early plates were obtained in the presence of a slight leak. Under the circumstances the magnitude of this leak becomes of importance. For example, the plate of the previous article was obtained with the surprisingly large leak of 0.2 mm. in an hour, showing that perfect tightness of the apparatus was not necessary when proper attention was given to washing with hydrogen. If, however, the receiver was to be exhausted below .1 mm. the leak must be very much reduced. Practice and care in setting the face plate secured this result and work has been done where the leak in 24 hours was less than .02 mm.

In those cases where the discharge tube is separated from the spectroscope by a fluorite window what has been said about the purity of the gas in the receiver and the

amount of washing necessary to secure it remains of course true. To this is now added the trouble of pumping and filling the discharge tube with whatever gas may be under examination. The gas in the discharge tube, however, may be used over a considerable range of pressure, for the presence of the fluorite window prevents the discharge from spreading into the spectroscope. In practice the pressures varied in different experiments from 2 mm. to .5 mm. The pressure in the receiver was usually reduced to 0.1 mm., though if the hydrogen be pure so low a pressure is not at all necessary. The width of slit used varied from .09 mm. in the case of the crude plate published in a former article to about .025 mm. in the case of the fine plates from which measurements have been made.

The time of exposure for the hydrogen spectrum varies between five and thirty minutes according to the width of slit and the sensitiveness of the plate.

DRY PLATES.

Little can be added to Schumann's description[3] of the manufacture of the special dry plates necessary in this work. The first part of the research was carried on with plates prepared from glass 1.5 to 2 mm. in thickness. When the form of the spectroscope was improved and it became necessary to bend the plates to the arc of a circle special sheets of thin glass were required. In order that the emulsion may flow evenly the plates must be very flat. This necessity of flatness together with the mechanical difficulties of grinding put a limit to the thinness of the sheets. In practice plates 8.8 × 13 cm. and between .4 and .5 mm. thick are flowed and when dry are cut into small pieces 2.6 × 4.4 cm.

One slight departure from the method of Schumann has been found advisable; each plate was separately supported on legs during the process of flowing. In this way if the emulsion run over the edge of one plate, only that plate is spoiled; while if all the plates are on one levelling table a disaster to one may result in the overflow of all.

In development the author has used ortol with good results. Here, as has been remarked by Schumann, the strength of the developer must be regulated by the age of the plate. The addition of ice is a very necessary part of the process. The following proportions are suitable to plates six months to a year in age: Ortol A, 1 part, B 2 parts, Water 2 parts, ice about 1 part.[4]

[3] Ann. der Physik. Vol. 5, p. 349. 1901.

[4]

A.		B.	
Water	1000 cc.	Water . .	2000 cc.
Metabisulphate of Potash	7.5 gr.	Pot. Carb.	120 grs.
Ortol	15 gr.	Sod. Sulphite	360 grs.
		Hypo. 1 to 20	20 cc.

ELECTRIC APPARATUS.

The electric apparatus used to excite the discharge tube has in almost all cases consisted of a transformer run from the 60 cycle 110 volt alternating circuit and provided with a suitable rheostat in the primary. When such a transformer is used with a discharge tube containing gas at pressures from 1 to .1 mm. the addition of capacity across the terminals of the tube produces — with most gases — very little effect on the nature of the discharge because the low resistance of the tube after the current has once begun to pass does not permit the condensers to charge. If a spark gap be introduced in series with the tube this difficulty is of course obviated. In all the earlier work no gap was used so the spectra obtained were due to a discharge practically without capacity. The capacity when introduced consists of glass plates coated with tin-foil and has a value of perhaps .005 microfarads. In some of the work a coil with a mechanical break taking 12 volts and 5 amperes in the primary has been substituted for the transformer. In the case of the metallic spectra used for comparison the spark has of course been brightened by the use of capacity.

METHOD OF TESTING FLUORITE.

In order to provide a window of the greatest possible transparency for the discharge tube, in those cases where the spectra of gases other than hydrogen were to be examined, it was necessary to test various specimens of fluorite which the author had at his disposal. The method was as follows: The piece under trial was attached to the plate-holder at the end of an arm in such a way that it projected to the right of the ways in which the holder moves. The length and shape of the arm was so adjusted that when the plate-holder was at its highest position the fluorite was just above the right hand slit, but when the holder had been allowed to fall the fluorite slab fell with it and came between the slit and the mouth of the discharge tube. The receiver was exhausted and filled with hydrogen in the usual way, rather a wide slit was used. A photograph was then taken with the plate-holder at its highest position, thus the light path lay entirely in hydrogen. Next, by means of the magnetic device, the plate-holder was allowed to fall until the specimen of fluorite came in front of the slit, the light from the tube now passed through the fluorite before reaching the slit. By comparing the two spectra, obtained one below the other on the same plate, the point in the spectrum at which the specimen cut off the light could be easily determined.

Six circular plates of white fluorite 3 mm. thick and 2.5 cm. in diameter, and two plates 2 mm. thick — all from Zeiss of Jena — have been tested, with the result that, while none of them are absolutely opaque to light below λ 1600, their transparency varies very much. In no case, however, was any line of wave-length shorter than λ 1200 obtained, and of the eight pieces but two showed this transparency. The abrupt nature of the absorption at this point is well shown by spectra II and III in Plate VIII. II was taken with the internal capillary discharge tube and fluorite window, III with no window between tube and slit. The author is not of course prepared to say that no fluorite does exist transparent to light below λ 1200, he can only say that of the best specimens obtainable up to the present, but two show even this limited transparency. The discovery of some substance transparent to light of the very shortest wave-length known to exist would be an important step. For our knowledge of the spectra of gases other than hydrogen is at present limited by the transparency of fluorite.

The effect of the thickness of the fluorite window was tested by taking a series of spectrographs through one of the two best specimens and then reducing the thickness of the piece from 3 to 0.9 mm. A second series taken through this thinner window showed no extension of the spectrum whatsoever. This is a result which might have been expected from the work of Schumann and which confirms, for this region, that slow increase of absorption with thickness which has been observed in other parts of the spectrum.

ABSORPTION OF THE AIR.

The absorption of the air is the important factor in all investigations which have to do with radiations of short wave-length. Cornu was the first to investigate the matter systematically, but Schumann has vastly extended the work and has given data on the relation of length of air path to the limit of the spectrum. His method was to interpose a cell whose thickness could be varied between his source of light and the slit of his spectroscope. This cell was filled with air at atmospheric pressure.

There is not much to add. The method here employed was as follows: The discharge tube was separated from the spectroscope by a fluorite window and spectrographs were taken with air in the receiver. Thus the light from the discharge tube traversed a layer of fluorite and then passed through air to the grating and back to the photographic plate — a distance of about 200 cm. By taking a series of spectrographs at different pressures the variation of the absorption with pressure could be

observed. At the very beginning of the investigation the author was confronted by a puzzling and persistent phenomenon — the absorption of the air appeared to be selective, not total. For a broad absorption band appeared between λ 1790 and λ 1550 and remained undisturbed even when the pressure had been reduced to .17 mm. At this point the air permitted the remainder of the spectrum to pass nearly down to the limit of transparency of the fluorite window. It was only after the receiver had been frequently washed with carefully dried air that the absorption band disappeared. The phenomenon is therefore due to some impurity — possibly something which comes from the brass of which the receiver is made, and which only persistent pumping will remove.

It is not perfectly satisfactory to compare the values obtained by Schumann, which are given in terms of the absorption of a column of air at atmospheric pressure, with those obtained by the author. It may be of some interest to point out, however, that, if the lengths of two equivalent air paths are to each other inversely as their corresponding pressures, the column of air in the receiver at .17 mm. pressure 200 cm. long is about equivalent to a column at atmospheric pressure 0.4 mm. in length. Now, when the receiver was at this low pressure, light of wave-length a trifle below λ 1400 was recorded on the photographic plate. It appears, therefore, that a column of air 0.4 mm. long will permit light of this short wave-length to pass in sufficient intensity to affect a photographic plate under the conditions of the experiment.

The expression of the absorption of the air in anything like an absolute system is a very difficult matter. The point of practical interest in this part of the research is the advantage of an atmosphere of hydrogen in the receiver. It is not easy to exhaust the apparatus to a sufficient degree of transparency, but by successive washings with hydrogen the last traces of air can be removed and its absorption very largely eliminated.

PURITY OF THE SPECTRUM.

The spectra of hydrogen, from which the wave-lengths recorded in the following tables were measured, have been obtained under some variety of condition, but they all show considerable uniformity of appearance. The greatest difference occurs between those spectra obtained from an internal capillary discharge tube closed by a window and those where the tube communicated directly with the receiver. Contrary to expectation the spectra obtained under the latter condition are much purer than those which the first method yields. No matter with what care the closed discharge

tube is pumped and repeatedly washed with hydrogen, certain characteristic bands are bound to make their appearance to a greater or less degree. The nature of these bands is unfortunately only too clearly seen in spectrum II of Plate VIII. If, however, the tube communicates directly with the receiver and is filled with hydrogen along with it, these bands may be totally absent. Schumann has observed their presence and ascribes them to carbon monoxide. On this point the author cannot yet be sure; certain it is, however, that they occur strongly in the spectrum of the air. (Compare spectra I and II, plate VIII.)

The means used to produce the hydrogen for the discharge tube have been varied. Zinc and hydrochloric acid, and electrolytic action in both dilute sulphuric acid and on barium hydrate solution have served as sources for the gas. Various shapes of discharge tube have been tried, both closed and communicating directly with the receiver. Aluminum, copper, and iron have been used as the material of the electrodes which in turn have been of various dimensions. The comparison of the plates taken under the above conditions serves as an excellent test of the true source of the radiations supposed to be due to hydrogen.

In addition, the spectra obtained by exciting the discharge tube when filled with air at pressures between 2 and .5 mm. have been compared with the spectra obtained when the same tube was filled with hydrogen. The lines found to be common to the two spectra have been eliminated as due to the air itself or to some impurity. Such a process may result in the loss of a few true hydrogen lines but what remain can be safely attributed to that gas. Finally, this matter has been checked by a study of the behavior of suspected lines as the purity of the hydrogen in the discharge tube is increased. It must be remembered that the elimination of lines due to impurities by comparison of the air and hydrogen spectra can only be applied to those radiations which lie in that region for which fluorite is transparent. The results are to be found in the table of wave-lengths given at the end of this paper.

The general appearance of the spectrum may be described as follows: Between λ 2000 and λ 1675 the author can find no trace of radiation due to hydrogen, but he is not prepared to assert that a faint continuous spectrum may not exist. From λ 1675, however, the spectrum consists of a multitude of very fine lines with a maximum of intensity near λ 1600. Near λ 1300 something very like an absorption band occurs, due, perhaps, to some slight trace of impurity in the gas, but always present no matter under what conditions the gas may be produced or examined. Lines are visible in this band but they are very feeble. The lines beyond the region limited by the absorption of fluorite are some of them as strong as any in the spectrum. The lowest

measured wave-length has the value λ 1030.8 but beyond this there are some very faint lines whose wave-length must be between λ 1000 and λ 1010. At present these lines form the limit of the spectrum.

The nitrogen-like appearance of the spectrum of air shown in fig. 1, Plate VIII deserves attention. The fluted bands are beautifully clear in the original negative and their general character can even be seen in the reproduction.

EFFECT OF CAPACITY ON THE SPECTRA.

The spectra both of air and hydrogen were obtained with no capacity in circuit with the discharge tube beyond that afforded by the connections of the apparatus. The effect of capacity on the spectrum of both gases in the visible is so striking, however, that it seemed worth while to study the phenomenon in this new region of short wave-length. Moreover, the recent attempts which have been made to extract from the change in spectrum with change in condition some evidence as to the nature of the vibrating system of electrons, make such experiments doubly interesting. For in this new region we are dealing with vibrations more than three times as rapid as those studied in the visible spectrum. This difference in rapidity might well be expected to differentiate the effect produced by a given change of condition on the visible spectrum from the effect produced by the same change on the region between λ 2000 and λ 1030. It is even possible to conceive that this differentiation might throw some light on the vibrating system itself.

The research is unfortunately beset with mechanical difficulties. Reference has already been made to the trouble experienced from the spreading of the discharge into the spectroscope and the resulting fog produced on the photographic plate. This difficulty is increased a hundred fold if a disruptive discharge is sent through the tube, for in this case the whole interior of the spectroscope seems to become luminous and a total fogging of the plate results. With great care as to regulation of pressure some spectrographs have been obtained, but they have never been perfectly satisfactory, since even if but a single spectrograph is taken on a plate the time of exposure must be short. When the investigator turns from the direct connected discharge tube to one closed from the receiver by a fluorite plate he is confronted by a new difficulty. The fog indeed is prevented, but after a short time the violence of the disruptive discharge deposits a thin film on the fluorite window and renders it totally opaque. This film need be hardly visible by transmitted light and yet it will be thick enough to absorb all wave-lengths below λ 1800. The material of the electrode exercises of course a pronounced influence, but even with aluminum, which shows the effect the least, the

result is as above described. The annoyance of disconnecting the discharge tube from its pump, removing the face plate from the receiver, detaching the discharge tube from the face plate and cleaning the window, followed by the same set of operations in the inverse order, must be experienced to be thoroughly appreciated. When it is remembered that with a disruptive discharge this process must be gone through after about four exposures the difficulty of this part of the research will be understood.

In practice the discharge tube was filled with hydrogen and a spectrograph taken without capacity, next a spark gap was introduced in series with the tube, and capacity was put in parallel until the gas showed the four line spectrum clearly. The appearance of the tube was constantly watched with a direct vision spectroscope.

A similar set of experiments were tried for air. In both cases the material of the electrodes was altered in various experiments. It is important to observe that the nature of the electrode does not seem to affect the nature of the phenomena.

The effect of the introduction of capacity with hydrogen is to introduce five sets of new lines. These lines lie between λ 1900 and λ 1400; under favorable circumstances they are strong and characteristic. The appearance of the principal spectrum remains unaltered, except for a very slight weakening.

The effect of capacity on the spectrum of air is very different. The band spectrum is weakened to such an extent as to be almost wholly destroyed and five sets of new lines are introduced. These new or secondary lines are identical with those which appear in hydrogen. Though some of these lines are always present both in hydrogen and in air, with the disruptive discharge, they vary very much in intensity from experiment to experiment. This variation with the condition of the research, added to the fact that the secondary lines appear both in hydrogen and in air make it almost certain that they owe their origin to some impurity common to both gases. The nature of this impurity can only be decided after the spectra of the other principal gases have been examined. At present it seems safe to state that (1) there is no secondary spectrum of hydrogen in the region below λ 2000; (2) that the introduction of capacity almost totally destroys even the primary spectrum of air; (3) that new and characteristic lines do come into existence, in both air and hydrogen, and that these lines are probably due to some impurity. In weighing the evidence here presented it must be remembered that these results have been checked by experiments performed under very varying conditions. The pressure and purity of the gases, the shape and character of the discharge tube, the material of the electrodes, and the time of exposure are all factors which have undergone investigation.

METHODS OF MEASUREMENT.

The methods used were two in number. The values of all the lines were first obtained by the two-slit method and these values were then checked by obtaining the stronger lines in the second spectrum and comparing their positions with known iron lines in the first spectrum. For this last purpose the first and second spectra obtained from the left hand slit were employed.

The two-slit method has been described elsewhere, but a brief account of its theory and its limitations may not be out of place here. If two slits, S and S', be placed on that circle whose diameter is the grating's radius of curvature, the illumination of these slits by white light will give rise to the images I and I'. To each of these images a set of spectra will correspond. For the present purpose it is sufficient to concentrate the attention on the two first spectra. It is evident that these two spectra will be shifted with respect to each other by an amount depending on the distance between the slits. If a photographic plate be placed between S and S', and if the height of these slits be properly adjusted, one of these spectra will be superposed upon the other. At a given point, P on the plate, the light brought to focus from S will be of a shorter wave-length than that from S'. If the sources of light be so selected that the wave-lengths in both spectra arriving at P have known values, then the shift of one spectrum with respect to the other may be determined by comparison of these values. If the apparatus is in adjustment both spectra are in focus upon the same circle and the amount by which one spectrum is shifted over the other is a constant quantity; that is to say, if the shift is determined by comparing known lines at one end of the plate, it must have the same value at the other end. It is upon this property that success in the use of method depends.

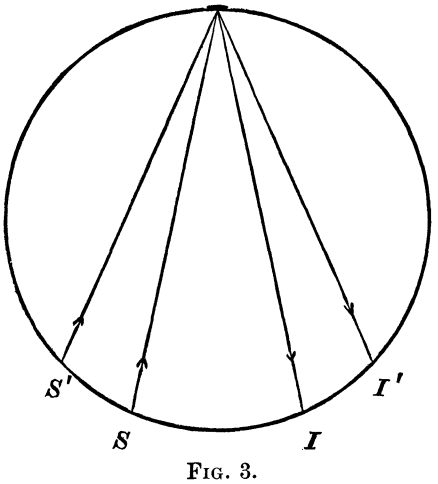


FIG. 3.

It next becomes of importance to inquire to what extent small errors of adjustment will influence the constancy of the shift. Here the nature of the method upon which the observer must rely in determining the perfection of this adjustment must be remembered. The only practical test consists in the sharpness of focus of the two spectra. It is the object then to so manage matters that both spectra shall be in perfect focus throughout the plate's length and at the same time. The vital question at

once suggests itself: Is this test sufficiently delicate for the present purpose? If very accurate results are required the question must be answered in the negative. A little consideration makes it obvious that the relative position of the images I and I', and hence the shift, changes with the focus more rapidly than can usually be detected by the change in sharpness of the lines. In other words, if the shift were given, the proper focus could be accurately determined, but if the sharpness of focus must be relied on, then the true shift can only be approximately inferred. Or again, for practical purposes, the apparent shift varies slightly more rapidly with variation in adjustment than does the sharpness of the spectral lines. The foregoing is, of course, somewhat dependent on the manner in which the adjustment is made. In the apparatus in question the slits and the photographic plate are rigidly fixed on the arc of a circle. This arc is capable of being thrust in or out parallel to itself along a line connecting the centre of the grating and the centre of the photographic plate; it is also capable of rotation about its middle point. By these two movements perfect adjustment can be attained, but the test of this adjustment is not absolutely adequate.

The practical application of the method is as follows: The spectrum of iron was selected for comparison work. The grating was so turned that known lines in the spectrum of aluminum fell upon one end of the plate when the right hand or direct slit was illuminated by light from a spark between terminals of the metal. The shift of the principal spectrum with respect to the comparison spectrum was then determined by comparing the positions of these lines in aluminum with known lines in the spectrum of iron. In order to insure accuracy this shift determination was recorded on the same plate as the spectrum of hydrogen whose lines were to be measured. This was conveniently brought about by admitting the light from the aluminum spark directly through the discharge tube, for which purpose the tube was fitted with a window of quartz at the end not attached to the face plate. Upon the spectrum to be measured was superposed the comparison spectrum of iron, and in this spectrum fiducial lines were selected. The relative value of these lines was then obtained by subtracting the shift from their real value, previously corrected to vacuum. These relative values were then used as points of departure to determine the wave-lengths of the unknown gas spectrum. In practice the shift was 1180 Ångström units so that the point in the iron spectrum falling on say λ 1400 of the gas spectrum has a value of 1400 + 1180 = 2580 Ångströms.

Owing to the dimensions of the plate only a region of about 760 tenth metres can be photographed at one time. Thus if the aluminum line 1935.29 falls upon one extreme of the plate the other end corresponds to wave-length λ 1175. In order to

investigate light of shorter wave-length than this value it is necessary to turn the grating, a process which necessitates a slight change in the adjustment of slits and plate.

To check the values obtained in the above manner lines of short wave-length were obtained in the second spectrum. For this purpose the left hand slit was covered by a discharge tube without a window and the whole apparatus was filled with hydrogen exactly as usual. Owing to the feeble character of the second spectrum only the stronger lines between $\lambda 1550$ and $\lambda 1200$ could be photographed. Their position was determined by comparison with first spectrum iron lines obtained from light which had passed directly through the discharge tube. The average difference between the values obtained by the two methods is 0.3 Ångström unit.

The plates have been measured on an engine made by Wolz of Bonn after the design by Kayser. The screw has been calibrated and proves to be of an accuracy far greater than this work demands. The intensities of the lines have been estimated, first, by observations made under the reading microscope, and, second, by projecting the spectrum on a screen. The latter method has the advantage that the whole spectrum is before the observer at one time. The values were estimated from plates taken without a fluorite window. The tables are divided into two parts. In the first are given 310 lines lying in that region from which it has been possible to eliminate the lines due to impurities. The error should not be greater than 0.3 Ångström. In the second are lines in that region beyond the transparency of fluorite; their origin is not absolutely known, but they are probably due to hydrogen, since they were obtained when the discharge tube was connected directly with the spectroscope, a condition under which air lines rarely occur. The error in these values should not be greater than one unit. The values of the iron lines are from the measurements of Exner and Haschek as given in Watts' Tables;[5] the correction to vacuum came from the same source. The wave-lengths of the aluminum lines are from the measurements of Eder and Valenta.[6]

The agreement between the tables and the numbers given in the "Preliminary Measurements" is well within the accuracy claimed for the earlier values.

SCHUMANN'S SPECTRUM.

In order to compare the prismatic spectrum obtained by Schumann with the values of the table the twelve plates published in the Smithsonian Memoir[7] were cut out and pasted together. The resulting spectrum, some 127 cm. long was placed upon a

[5] Index of Spectra, W. M. Watts, Appendix J.
[6] Beiträge zur Photochemie, p. 388.
[7] Smithsonian Contributions, No. 1413.

movable stand and the grating spectrum was projected upon it by means of a lens. By changing the magnification so as to keep step with the dispersion the strong lines on the one spectrum were identified with those in the other from λ 1674 to λ 1269 without the least difficulty. From the values thus obtained interpolation curves were drawn for each one of the twelve plates separately and by means of these curves a scale of Ångström units was attached to each of the twelve illustrations. By the permission of Dr. Schumann and through the kindness of Professor Langley of the Smithsonian Institution the half-tone reproductions which appear at the end of this memoir were then made from these illustrations. They by no means do justice to the fine originals, but considering the difficulty of the process they may be considered fairly satisfactory.

The agreement between the author's measured values and the prismatic lines is extremely gratifying. Of the two hundred and eighty-five lines given in the tables all but three or four are found in Schumann's plates. There are, however, a considerable number of fainter lines in the prismatic spectrum not visible in the plates obtained with the grating. Moreover, owing to the fineness of the slit, and the great dispersion used by Schumann some of the single lines of the table are seen by comparison with the prismatic spectrum, to consist of doublets or triplets.

The excellent agreement between these two spectra obtained under such different conditions makes the existence of any chance impurity very improbable.

The extreme line in Schumann's map has the value λ 1266.9. That author has stated that he obtained some lines too faint to reproduce; from the angles given [8] it is difficult to calculate their exact wave-length, but it seems improbable that they should have a value much below λ 1230. In this connection it is interesting to note that the calculation of Martins [9] from the Kettler-Helmholtz formula for fluorite was not far wrong.

LIMIT OF THE SPECTRUM.

It may well be asked, — to what is the present limit of the spectrum due? There are several causes which go to make up an answer to this question.

A much longer exposure might result in the discovery of new lines; unluckily there are difficulties in the way of this seemingly simple step. For, as has been previously stated, with a windowless tube there is a great tendency for the discharge to spread into the receiver and cause fatal fogging of the plate. No plan has so far been devised to obviate this difficulty and up to the present the length of exposure has

[8] Smithsonian Contributions, 1413, p. 24.

[9] F. F. Martins Ann. der Physik, 1901. Heft II., p. 619.

been limited by it. Besides this mechanical difficulty several other possible agents may exert an influence. Speculum metal may cease to reflect in the region near λ 1000 ; that it reflects so well down to this point is surprising. The Schumann plates may cease to be sensitive. Small impurities in the hydrogen may exercise considerable absorption. Only experiments on metallic reflection, on the manufacture of plates and on the purification of gases can answer these questions. The author sees no insurmountable difficulty, however, to the still further extension of the spectrum.

RESULTS.

The results arrived at in this memoir may be set forth as follows:

I. The spectrum has been extended from the limit obtained by Schumann to the value λ 1030.

II. The lines in the spectrum of hydrogen have been measured accurately from λ 2000 to λ 1228, and the values of the principal lines to λ 1030 have been determined.

III. The nature of the spectrum of air has been investigated.

IV. The limit of transparency of certain specimens of white fluorite has been obtained.

V. The effect of the disruptive discharge on the spectra of hydrogen and air has been studied, and the absence of a secondary spectrum of hydrogen established in the region below λ 2000.

VI. Wave-lengths have been attached to the spectrographs obtained by Schumann.

Much of this research has been carried on with the help of a grant from the Bache Fund. The permission to reproduce the plates from the Smithsonian Contributions is due to the kindness of the Secretary of that Institution.

It is impossible to conclude this memoir without some tribute to the man whose name will be always associated with the region of short wave-lengths which he discovered, and it is with the greatest pleasure that the author acknowledges the help and inspiration he has received from the friendship of Dr. Victor Schumann.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, Dec. 27, 1905.

SPECTRUM OF HYDROGEN.

MEASURED BY A DIFFRACTION GRATING.

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1228.3	8		1302.5	2	double	1380.2	5		1452.0	3	
1230.1	8		1307.5	2		1380.8	1		1452.5	1	
1231.0	1		1311.1	2		1382.9	1		1454.3	1	
1232.1	5		1312.9	2		1383.0	1		1455.1	7	double
1234.3	4		1314.7	1		1384.2	1		1456.3	4	
1235.8	6		1315.6	1	double	1385.6	2		1457.4	6	
1239.6	3		1319.2	4		1386.3	3		1458.4	6	
1241.5	2		1323.4	5		1387.7	4		1460.1	5	double
1246.1	4		1325.0	5	double	1390.0	1	double	1461.0	4	
1247.2	4		1327.1	3		1391.2	1		1462.0	3	
1248.0	2		1327.5	2		1393.2	3		1462.9	4	
1249.8	3		1329.3	1		1394.0	7	double	1463.9	8	
1251.2	3		1331.3	6		1395.2	2		1465.2	3	
1253.2	6		1333.9	8	double	1396.4	7		1467.2	6	double
1253.9	5		1335.3	2		1397.5	6		1468.6	6	
1255.5	4		1336.1	8	double	1398.0	1		1471.0	3	
1257.1	4		1337.6	6		1399.0	7		1472.5	3	
1258.2	4		1338.7	7	double	1400.6	1		1473.9	5	
1259.9	4		1340.9	1	double	1402.0	4		1474.9	4	
1261.9	8		1342.4	8		1402.8	8		1476.4	4	
1264.0	1		1343.6	1		1404.3	5		1477.3	3	
1264.6	5		1345.4	8	double	1405.5	2		1478.9	2	
1265.8	4		1347.2	9	double	1407.3	7		1479.7	4	
1267.3	1		1349.1	2		1408.6	3		1480.4	4	
1268.3	1		1350.2	3		1410.5	8	triple	1481.7	5	
1269.1	3		1350.8	3		1411.8	1		1482.1	1	
1269.9	1		1352.5	8		1413.0	8		1483.7	3	
1270.7	4		1353.6	8		1414.9	2		1486.1	1	
1271.5	4		1355.5	7		1416.4	3		1486.9	9	
1272.0	1		1357.3	6		1419.5	2		1487.8	1	
1273.3	3		1358.2	4		1420.3	3		1489.3	6	
1274.2	1		1359.2	5		1426.8	3		1489.9	3	
1275.0	3		1360.1	5		1427.8	7	double	1491.9	7	
1276.1	1		1362.4	1		1429.0	3		1492.7	1	
1277.1	6	double	1363.4	8		1430.1	7		1494.1	3	
1279.0	1		1364.3	3		1431.1	3		1495.5	10	double
1279.8	5		1365.8	5		1433.0	8	double	1499.8	8	
1281.2	4		1366.5	1		1434.3	3		1502.2	2	
1282.6	1		1367.6	3	double	1435.2	4		1503.9	1	
1283.4	6		1368.0	3		1436.3	7	double	1505.0	8	
1284.5	5	double	1369.1	1	double	1438.0	4		1505.9	1	
1286.9	5	double	1370.4	2		1439.1	1		1506.6	1	
1288.1	4		1371.3	6		1441.0	8		1511.5	8	
1289.4	3		1372.1	1		1442.8	1		1513.6	7	
1290.4	5		1372.9	3		1443.6	7		1515.0	6	
1291.3	2		1374.0	1		1445.2	4		1516.4	5	
1293.6	6	double	1374.5	2		1446.2	6		1517.5	6	double
1295.7	2	double	1375.5	1		1447.4	2	?	1519.0	6	
1297.4	5		1376.1	1		1449.2	2		1520.1	5	
1299.5	1		1377.2	6	double	1450.3	5		1521.7	2	
1300.0	3	double	1378.0	1	double	1451.0	1		1522.5	2	

SPECTRUM OF HYDROGEN. — *Continued.*

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1523.4	8		1556.4	2		1599.4	6		1625.8	4	
1525.4	5		1557.4	1		1602.0	8		1627.6	1	
1526.6	2		1558.7	1		1602.8	1		1628.5	8	
1527.5	4		1560.0	1		1603.8	1		1631.7	2	
1529.7	3		1561.1	2		1604.6	6		1633.7	6	
1530.9	6		1562.2	4		1605.3	5		1634.1	4	
1532.1	6		1563.0	1		1606.3	5		1635.3	3	
1533.2	6		1564.0	1		1607.7	10		1636.5	7	
1535.0	6	double	1565.1	3	double	1608.2	6		1638.2	4	
1536.7	1		1567.1	5	double	1608.6	10		1639.1	5	
1537.5	7	double	1569.2	6		1609.2	3		1639.7	1	
1539.2	5		1569.7	1		1610.1	2	triple	1640.5	6	
1539.9	2		1571.3	1		1610.5	7		1641.6	5	
1540.6	2		1571.7	7		1611.2	1		1643.0	5	
1541.6	7		1574.3	5		1611.8	3		1644.6	7	
1543.9	2		1577.2	8		1612.5	1		1645.7	2	
1544.7	8		1579.2	4		1613.3	7		1646.0	1	
1545.5	2	double	1581.0	7	double	1614.3	4		1647.8	1	
1546.4	6		1584.1	7		1615.0	3		1651.8	1	
1547.4	7	double	1585.7	7	double	1616.7	6		1654.2	2	
1548.3	1		1587.6	3		1617.9	1		1662.9	1	
1549.9	7	double	1589.0	8	triple	1619.9	2	double	1667.4	2	
1550.6	7	double	1590.9	4		1621.1	7	double	1670.2	1	
1551.5	2		1591.5	8		1622.1	3		1671.6	2	
1553.3	10		1593.6	7		1623.2	2		1672.4	2	
1554.9	3		1595.2	1		1623.8	7		1674.6	1	
1555.6	1		1596.2	10							

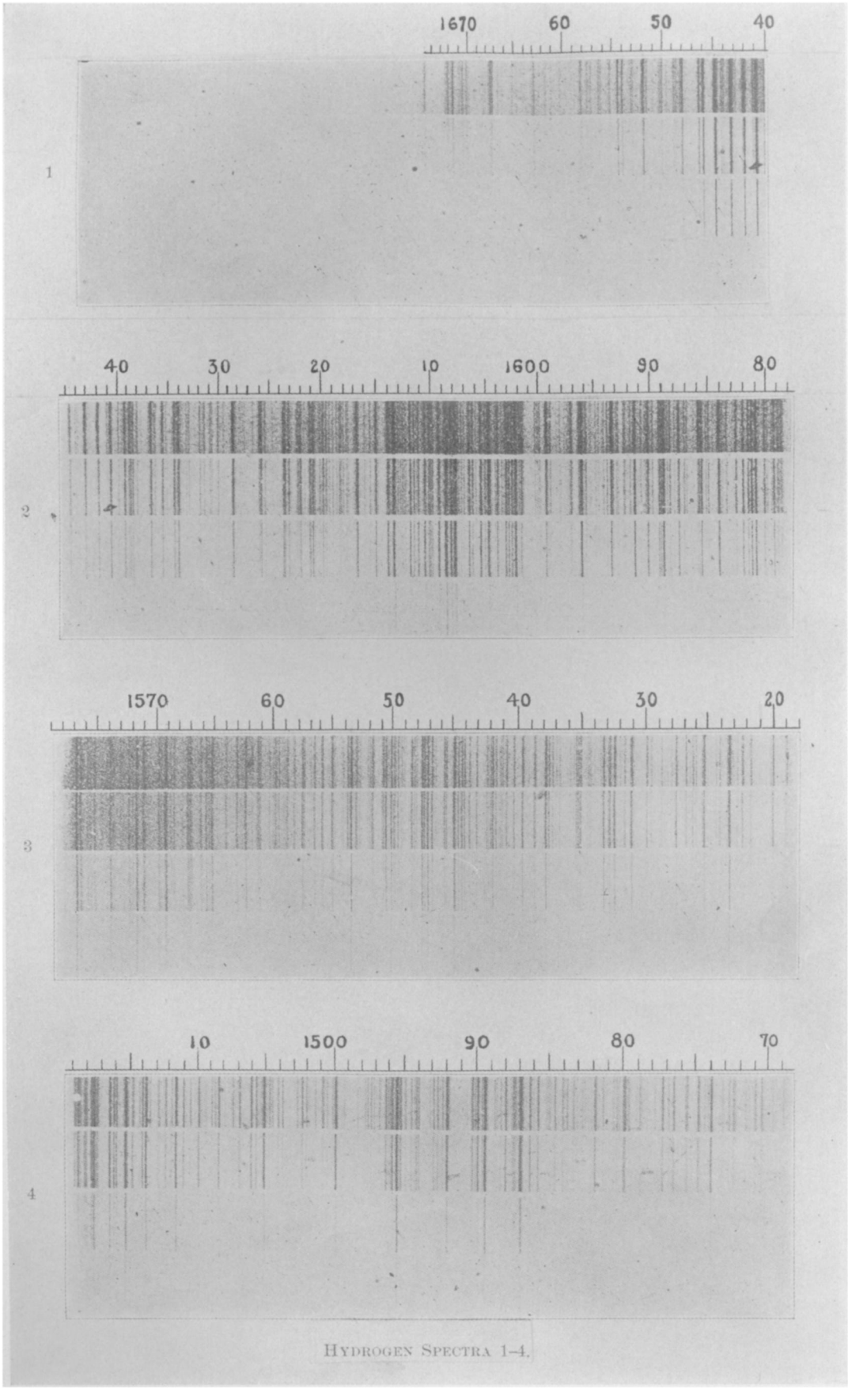
LINES OF UNCERTAIN ORIGIN.

Probably Due to Hydrogen.

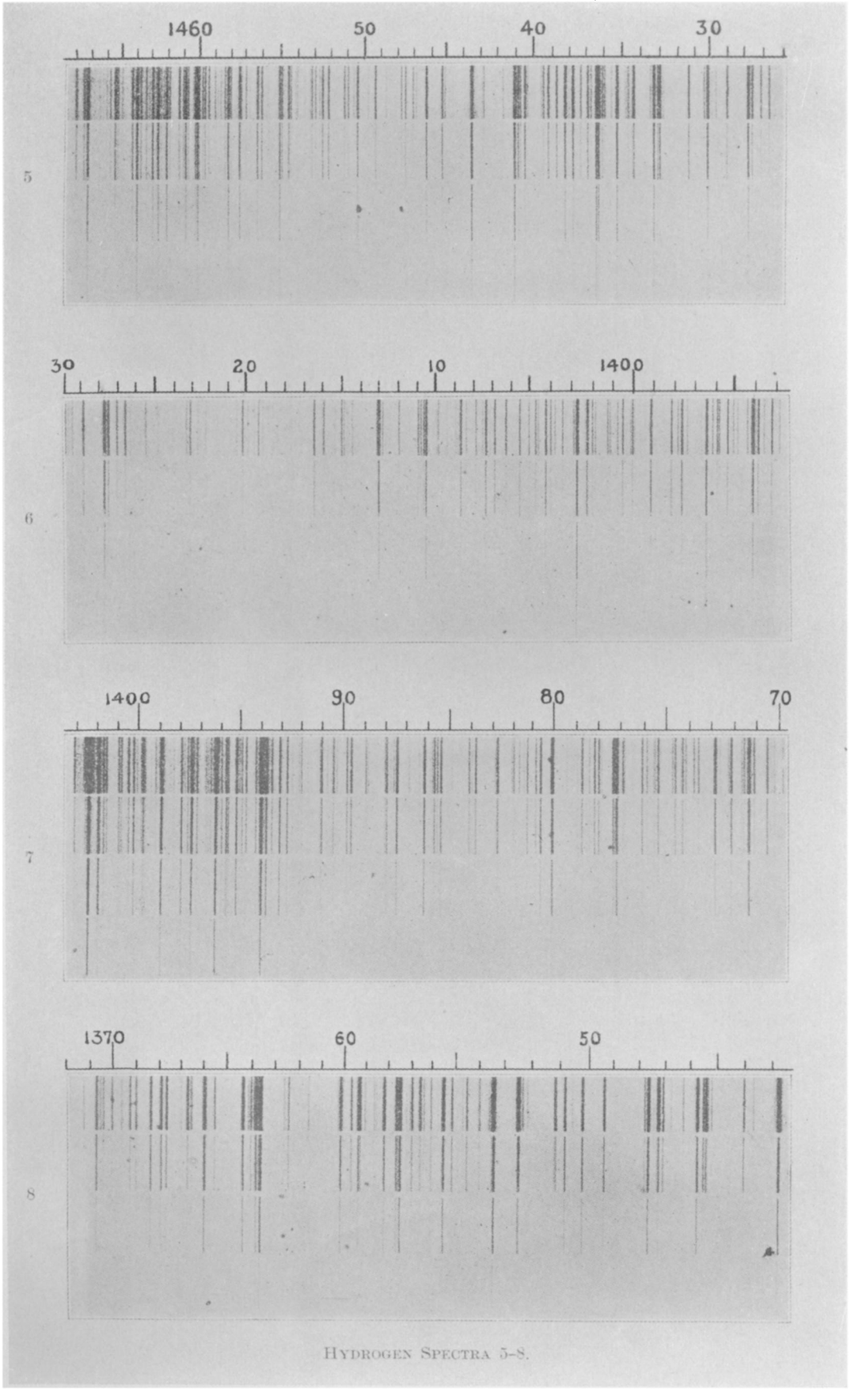
Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1030.8	1		1104.8	6		1176.2	5	double	1209.2	6	
1034.2	2		1107.5	6		1178.5	3	double	1209.7	1	
1045.2	4		1110.5	3		1180.8	7		1210.8	2	
1047.5	5		1119.4	4		1182.7	4		1211.7	3	
1062.1	1		1145.5	8	double	1185.0	2		1215.0	2	
1065.6	3		1148.8	2		1189.0	7	double	1216.0	8	
1070.0	1		1151.2	2		1198.6	2		1217.6	3	
1080.0	1		1160.9	10	double	1200.2	2		1219.1	1	
1082.1	1		1164.0	6		1201.8	3		1221.5	1	
1094.9	2		1166.5	6		1202.8	1		1223.7	3	
1098.0	2		1169.2	1		1205.2	6		1225.2	1	
1100.0	3		1172.6	1		1206.9	6		1225.9	7	
1102.2	4		1174.9	1		1207.8	2		1227.5	1	

PLATE III.

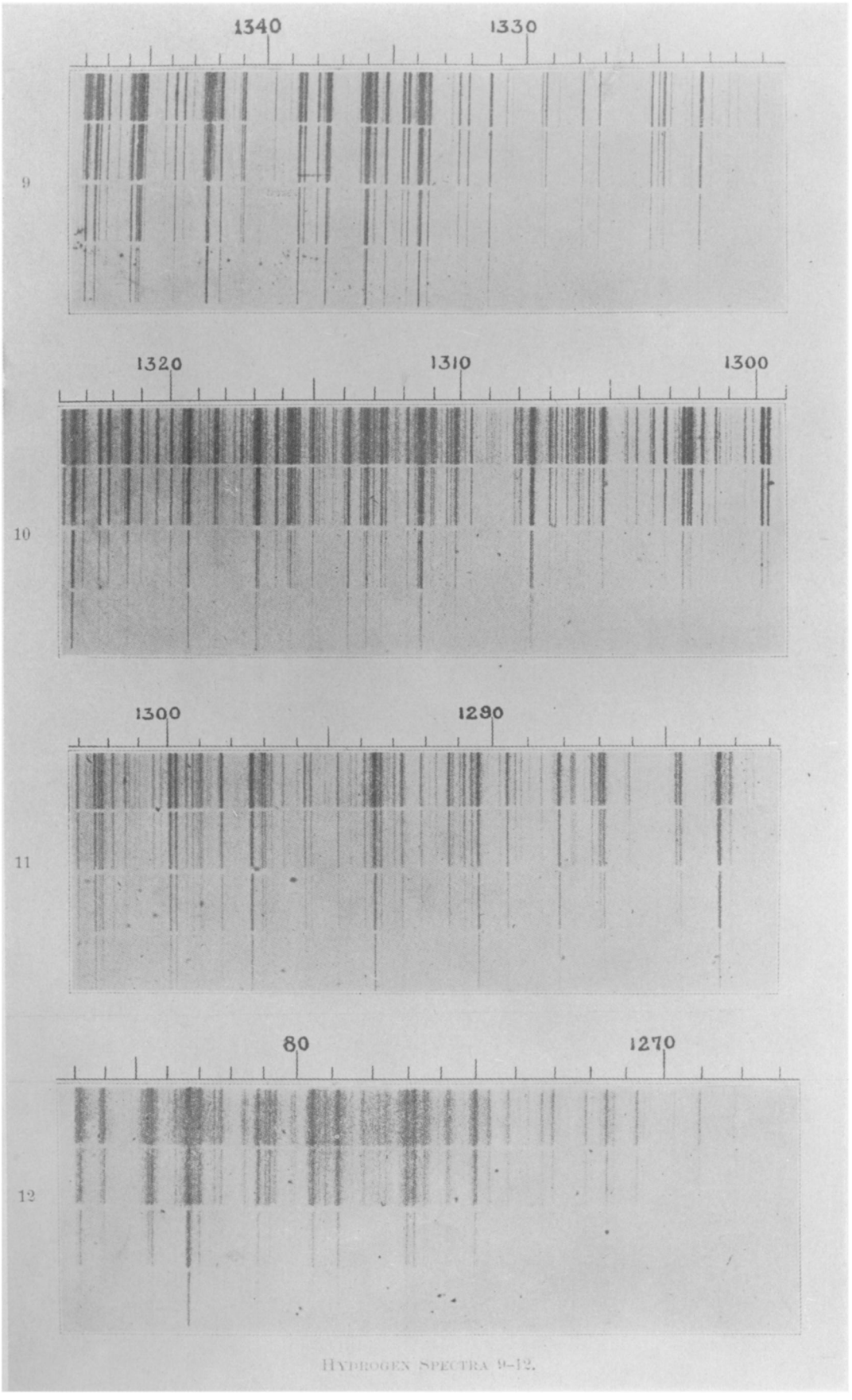
Reproduction of Schumann's hydrogen spectrum from the Smithsonian Contributions to Knowledge No. 1413, with a scale of wave-lengths from the author's measurements.



HYDROGEN SPECTRA 1–4.



HYDROGEN SPECTRA 5–8.



HYDROGEN SPECTRA 9–12.

FIG. 1.

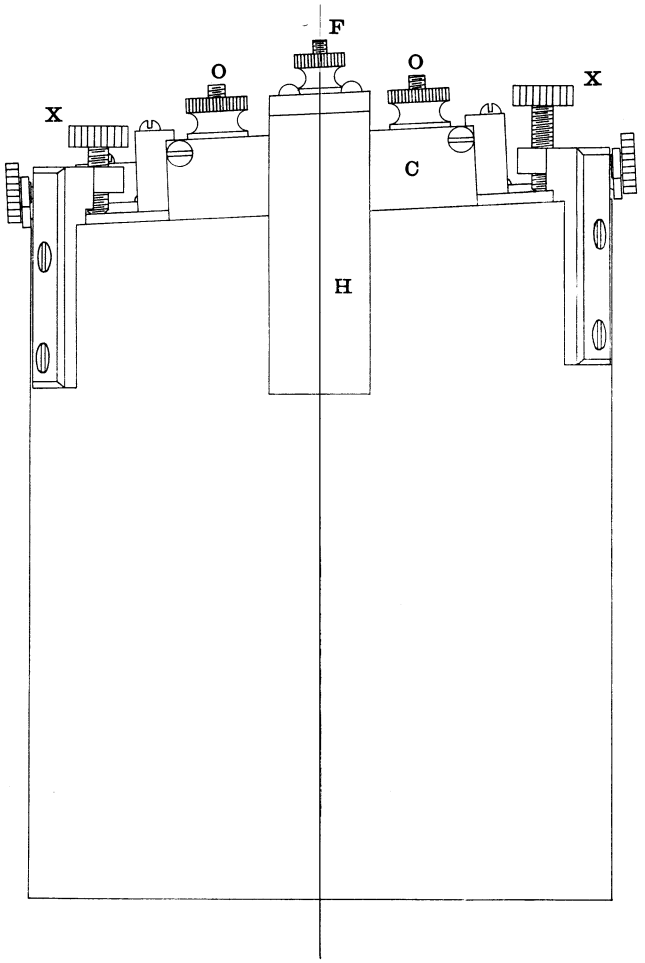
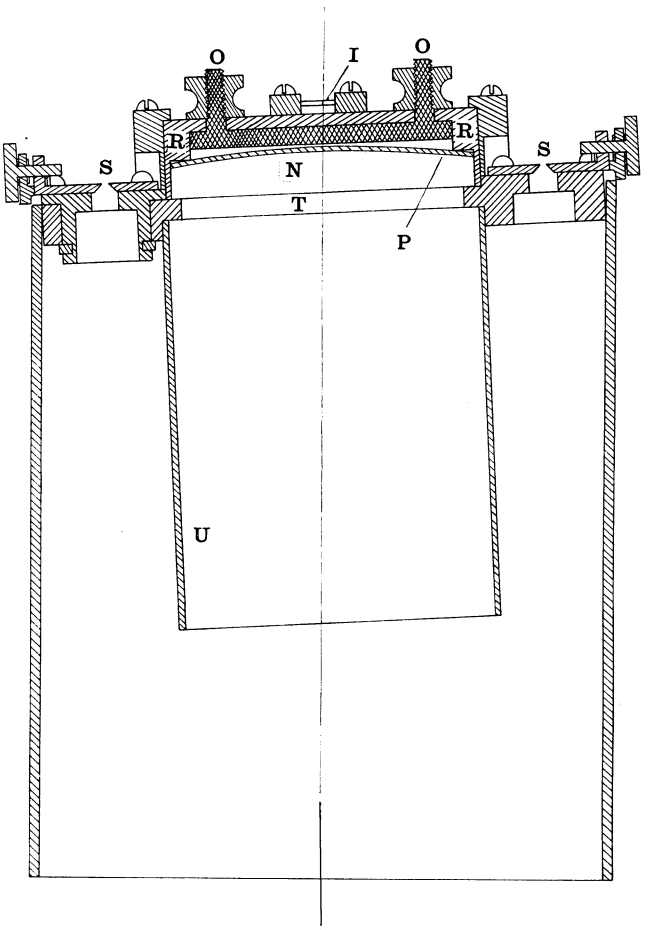


FIG. 2.



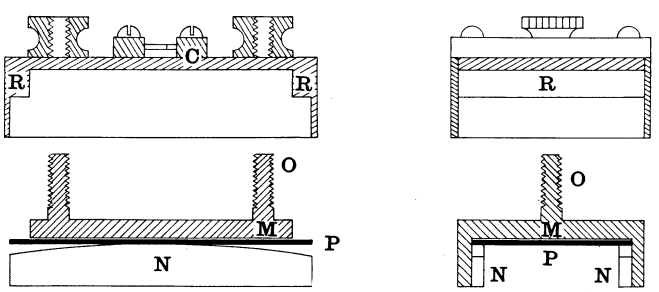


FIG. 3.

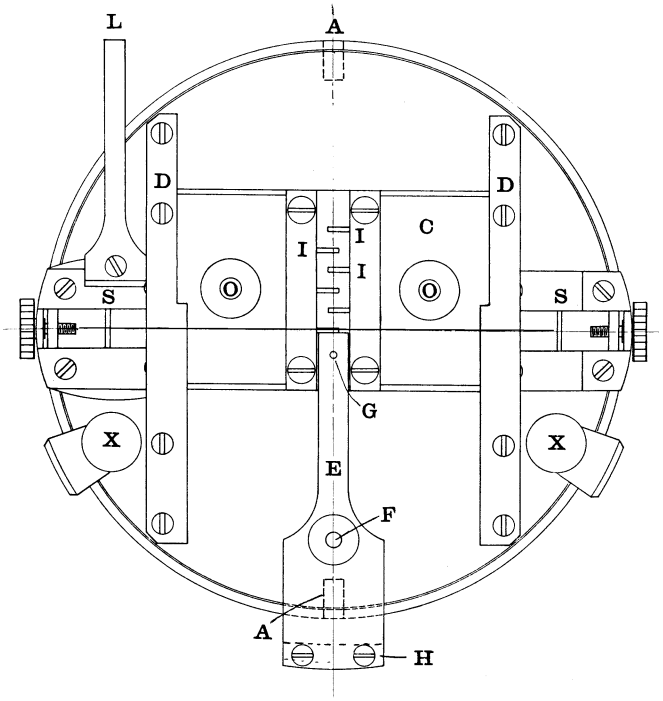
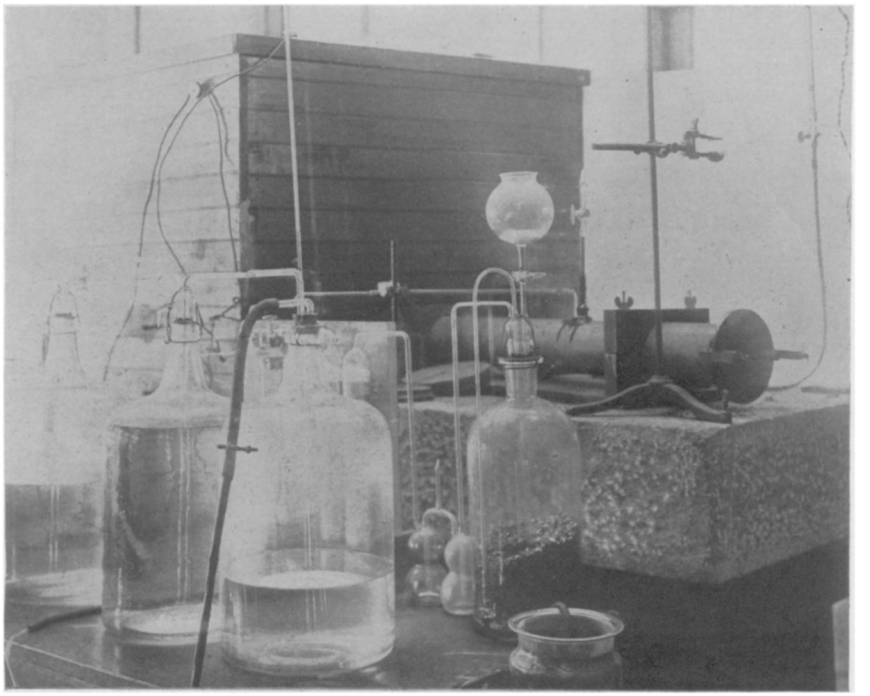


FIG. 4.

FIG. 1.



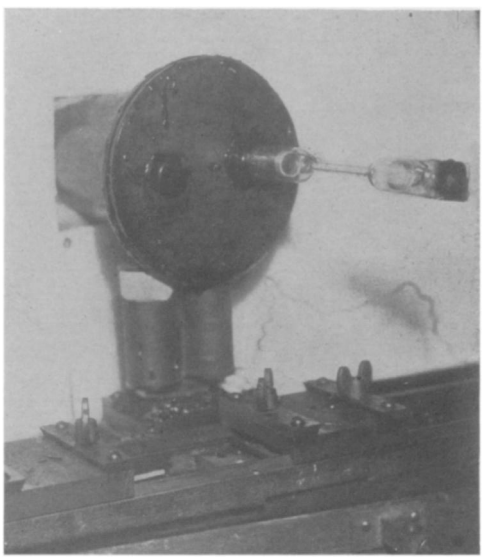


FIG. 2.

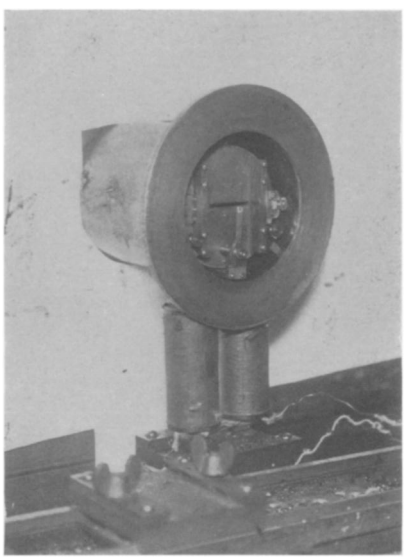


FIG. 3.

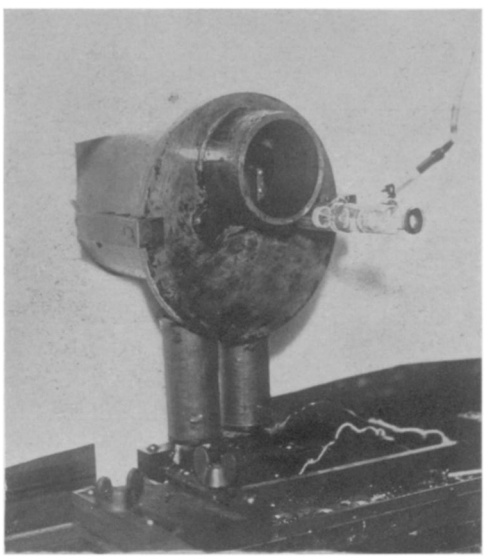
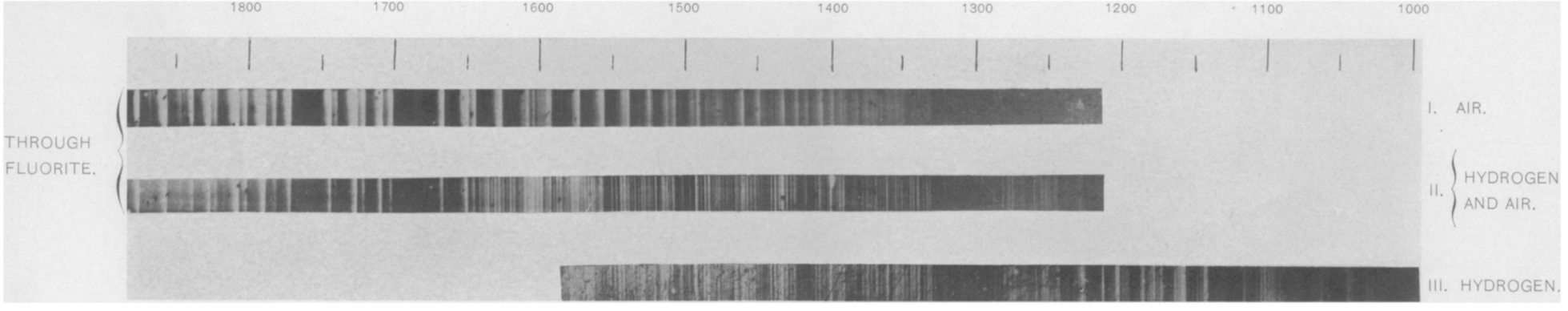


FIG. 4.



ABSORBTION OF FLUORITE.